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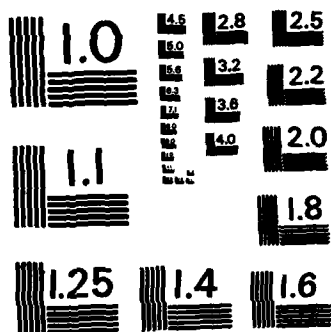
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High Temperature Electrothermal Processing--

Zinc from Zinc Oxide

by

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HIGH TEMPERATURE SOLAR ELECTROTHERMAL PROCESSING--

ZINC FROM ZINC OXIDE

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(Received September 22, 1982)

Abstract--We examined the feasibility of using sunlight to reduce the amount of electric power and/or fossil fuel needed to win metals from their ores and other compounds. The uniqueness of highly concentrated sunlight as a source of high-temperature process heat makes it attractive. We also examined, in some detail, ZnO as a candidate substance for exploratory experimental studies. We have mapped out, in temperature-pressure coordinates, the properties of the working substance and the thermodynamic performance of an archetype device as a guide to the temperature-pressure regime in which experimental studies might most profitably be undertaken.

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## INTRODUCTION

If a chemical transformation is to take place at a given temperature and pressure, the total amount of energy which must be added to the system is the enthalpy change,  $\Delta H$  of the reaction. However, heat addition alone may not be sufficient to effect the transformation. Energy in the form of electrical work or the use of its equivalent, a reducing agent such as carbon, may be required. The amount of electrical work needed for electrolysis is  $\Delta G$ , the change in the Gibbs function of the chemical reaction. The total energy which must be supplied,  $\Delta H$ , is thus the sum of the electrical work,  $\Delta G$ , and the process heat,  $Q$ . As electrolysis proceeds, the cell exchanges heat with the surroundings in the amount  $Q = \Delta H - \Delta G$  to maintain its temperature constant. The standard enthalpies and Gibbs free energies of formation of stable metallic oxides are large negative numbers.

The variation of  $\Delta H$  of a chemical reaction with temperature depends on the difference between the heat capacities of its products and reactants, which is usually small.<sup>1</sup> But the variation of the Gibbs free energy of a chemical transformation with temperature depends on  $\Delta S$  of the transformation (see Ref. 2, p. 162) which is often a larger positive number, especially if the reactant is a condensed phase and a product is a gas such as oxygen. While the enthalpies of formation of many metallic oxides are almost independent of temperature, their Gibbs free energies of formation decrease with temperature. Thus the electrolysis of such ores requires that an ever decreasing fraction of the energy required need be furnished as electric power as the temperature is raised; the rest can be process

heat from a baser source. For example, in the Hall process for the production of aluminum from aluminum oxide, process heat is supplied, unnecessarily, as electric power and from the combustion of a graphite electrode.

It is attractive to contemplate on how process heat supplied from sources other than electricity, which, from second law considerations, is energy in one of its most useful forms, might be used to reduce the consumption of this most valuable resource.

The sine qua non for such a process is a source of high-temperature process heat. Nuclear reactors might conceivably be used to moderately high temperatures. The maximum adiabatic flame temperatures of fossil fuels burning in air are about 2300 K.<sup>2</sup> With heat abstraction, the temperatures are much lower. Combustion per se is not a good source of high-temperature process heat. But highly concentrating solar collectors can be excellent sources at very high temperatures.<sup>3</sup>

It is therefore appropriate that the feasibility of using solar-augmented high-temperature electrolysis to produce metals from their salts, e.g., oxides, sulfides, and halides, be studied and that the thermodynamic boundaries within which such processes can be made to work beneficially be established. We report the results of a preliminary study of the recovery of Zn from ZnO.

# SOME PRELIMINARY OBSERVATIONS ABOUT ZINC OXIDE

For the reaction



$\Delta H = 348.3 \text{ kJ}$  and  $\Delta G = 318.4 \text{ kJ}$  at  $298.15 \text{ K}$ .<sup>4</sup> Thus, the production of one gram mole of solid Zn from solid ZnO or from a saturated solution of ZnO in a suitable electrolyte would ideally require, at room temperature, the input of  $318.4 \text{ kJ}$  of electrical energy. At the same time, the system would take up  $29.9 \text{ kJ}$  of process heat from the surroundings.

At  $1000 \text{ K}$ , which is above the melting point of Zn, the products are liquid Zn and  $\text{O}_2$ . The enthalpy change of this reaction is  $353.1 \text{ kJ}$ , about  $5 \text{ kJ}$  more than the room temperature value. But  $\Delta G$  is only  $246.4 \text{ kJ}$ . Thus, at  $1000 \text{ K}$ , in a suitable electrolyte,  $246.4 \text{ kJ}$  of electrical energy and  $106.7 \text{ kJ}$  of process heat would be needed to produce one mole of liquid Zn. The amount of electrical energy needed to effect the transformation at  $1000 \text{ K}$  rather than at  $298.15 \text{ K}$ , ideally, would have gone down by  $72 \text{ kJ}$ ; the amount of process heat would have gone up by  $76.8 \text{ kJ}$ .

Above the triple point temperature of ZnO (about  $2250 \text{ K}$ ) the amount of electrical energy required is essentially the work of unmixing the vapors, only about  $19 \text{ kJ}$  of electrical energy, 6% of the room-temperature requirement. The amount of process heat is  $449 \text{ kJ}$ .

Figure 1 shows the total energy ( $\Delta H$ ) the amount required as electric power ( $\Delta G$ ) and the process heat ( $Q$ ) required to produce the elements in their standard states from solid ZnO in an ideal process, as a function of the process temperature ( $T$ ). At temperatures below  $692.7 \text{ K}$ , Zn is a solid. It is liquid in the range  $692.7$ - $1180 \text{ K}$  and gaseous at higher

temperatures.<sup>4</sup> The temperatures at which vaporization occurs depend on the pressure. There is, therefore, a broad range of temperatures and pressures over which such a process could, in principle, be made to work. We have used an idealized archetypal model to gain insights into what would be the operating characteristics of such a process in various parts of the temperature-pressure regime.

#### THE ARCHETYPAL MODEL

Figure 2 is a schematic diagram of an archetypal device for producing Zn and  $O_2$  from ZnO by high-temperature, solar-augmented electrolysis. It is similar in many respects to idealizations we have used to evaluate other solar-thermochemical processes.<sup>3,5-10</sup> We assume that there are no frictional pressure losses in the system. Electrolysis takes place reversibly and isothermally. Process heat is supplied by sunlight. Although the electrolysis is reversible, the addition of process heat need not be. If the ZnO emerging from the heat exchanger at station 1 is at a temperature below  $T_h$ , the addition of process heat to bring it up to the temperature of the electrolysis cell is an irreversible process and will result in the production of entropy in the cell. Such heat addition takes place in a region between station 1 and the entrance to the electrolysis cell itself, designated station i, but not shown in Fig. 2.

Our heat-exchanger is large; although the descending streams are hotter than ascending stream everywhere in the heat-exchanger, the temperature difference may approach zero in some small part of the heat-exchanger. It never becomes negative, however.

We have assumed that the only species which need be considered are gaseous  $O_2$ , solid, liquid and gaseous Zn, and solid and liquid ZnO. The phase transformations are presumed to be fast enough so that the phases present are the thermodynamically stable ones. Inasmuch as ZnO vaporizes to the elements, ZnO vapor need not be considered as a separate species.<sup>11</sup>

Finally, we postulate that our fuel-cell operates isothermally and reversibly at ambient temperature. The power required by the electrolysis cell is taken as a debit on the fuel cell. The balance, the net power of the system, is identified with the amount of Zn produced.

Our model has three degrees of freedom and we may thus specify three operating variables. Once these variables have been specified, the operating condition of the device is fixed. We chose to vary the temperature of the electrolysis cell ( $T_h$ ) over the range 1500-2500 K, the pressure (P) over the range 0.01-100 atm, and fix the molar feed rate of ZnO at 1 mole per second.

#### OPERATING REGIME

The nature of the materials entering and leaving the electrolysis cell depends on its temperature and pressure. If the pressure were below the dissociation pressure of ZnO at the reactor temperature, for example, the feed stream would vaporize; it would become a mixture of Zn and  $O_2$  vapors. If the pressure were greater than the vapor pressure of Zn at the temperature of the reactor, the product would be a condensed phase of Zn; if it were less, the product would be Zn vapor.

Using the appropriate thermodynamic properties of ZnO,<sup>4,11</sup> Zn<sup>12</sup> and  $O_2$ ,<sup>13</sup> we constructed Fig. 3, a map of the various regions within the operational regime we have chosen to examine. The dashed line which separates Region I

from Region II is the dissociation pressure curve for ZnO. The dashed line which separates Region III from Region II is the vapor pressure curve of liquid Zn. The dashed line which divides Region II into IIa and IIb is the melting point of ZnO.

Thus, in Region I, the temperature is above the dissociation temperature of ZnO and much higher than the boiling point of Zn. Zinc oxide in the feed would therefore have vaporized before having entered the cell. It might have been incorporated into a condensed phase by having been added to an electrolytic solution which makes use of a higher boiling substance as a solvent. The product Zn would, of course, be produced as a vapor and would bubble from the cell as such.

In Region III, the feed is solid ZnO and the product Zn is a liquid.

In Region IIa, the feed is solid ZnO; the product is Zn vapor. In Region IIb, the feed is liquid ZnO; the product is Zn vapor.

Figure 3 shows that, at atmospheric pressure, ZnO vaporizes at about 2250 K, which is very near its triple point. Operation with pure ZnO at or above this temperature would therefore require that the electrolysis be conducted at elevated pressures, since the vapor phase around the electrodes would have to contain at least 1 atm of ZnO, in addition to the partial pressure of the products, which would both be gases. The advantage of operation in Region IIb is that the use of higher temperatures would obviate the need for a solvent since ZnO would be a liquid.

Operation at subatmospheric pressures and at lower temperatures might be facilitated by the use of solutions of ZnO in nonvolatile solvents. Liquid Zn would be produced as a product only in the region

above the Zn vaporization line. As we shall see when we deal with the thermodynamic efficiency of the process, there is a thermodynamic advantage to be achieved in producing liquid Zn rather than Zn vapor in the electrolysis cell, because Zn vapor causes a bad mismatch in the counter-current heat exchanger and a concomitant production of entropy. But the thermodynamic advantage of producing Zn liquid rather than vapor may be counterbalanced by rendering the search for electrode materials and the collection of Zn easier if it is produced as the vapor rather than the liquid.

### THERMODYNAMIC CALCULATIONS

In the equations which follow,  $\dot{n}$  refers to molar flow rate,  $\dot{W}$  to power, and  $\dot{Q}$  to heat flow rate. The subscript h refers to the temperature of or a condition associated with the electrolysis cell, 1 to the fuel cell; Roman numerals refer to the operating regions of Fig. 3 and Arabic numerals to the stations of Fig. 2.

#### Fuel Cell Power

The fuel-cell operates reversibly at 298.15 K. It uses solid Zn, which enters at station 4x, and  $O_2$ , which enters at station 4y. The power output of the cell is

$$\dot{W}_1 = \dot{n}_{ZnO,5} (0.5RT_1 \ln P - \Delta G_{ZnO,s,298}^{\circ}) \quad , \quad (1)$$

where  $\dot{n}_{ZnO,5}$  is the molar flow rate of ZnO at station 5,  $\Delta G_{ZnO,s,298}^{\circ}$  is the standard Gibbs free energy of formation (-318.36 kJ) of ZnO at 298.15 K, R is the gas constant,  $T_1$  is the ambient temperature (298.15 K) and P is the pressure.

### Power Required for the Electrolysis

The electrical work supplied to the electrolysis cell is the difference between the Gibbs free energies of the products and reactants. The power depends on the operating regime as follows:

$$\dot{W}_{h,I} = 0.9548 \dot{n}_{ZnO,5} RT_h, \quad (2)$$

$$\dot{W}_{h,II} = \dot{n}_{ZnO,5} (1.5RT_h \ln P - \Delta G_{ZnO,c,Th}^0), \quad (3)$$

where  $\Delta G_{ZnO,c,Th}^0$  is the standard Gibbs free energy of formation of condensed ZnO from Zn vapor and  $O_2$  at the electrolysis temperature, and

$$\dot{W}_{h,III} = \dot{n}_{ZnO,5} (0.5RT_h \ln P - \Delta G_{ZnO,c,Th}^0 - \Delta G_{Zn,g,Th}^0), \quad (4)$$

where  $\Delta G_{Zn,g,Th}^0$  is the standard Gibbs free energy of formation of Zn vapor from liquid Zn at the electrolysis temperature.

### Process Heat<sup>14</sup>

The process heat required by the electrolysis cell depends on the temperature at which the feed stream issues from the heat exchanger. In the present study, we permitted the temperature difference between the heated and cooled streams to approach zero at one point in the heat exchanger; at all other points, the temperature difference is great enough so that there is substantial heat exchange. The process heat in each of the three operating regimes is given by

$$\dot{Q}_{h,I} = -\dot{n}_{ZnO,5} \Delta H_{ZnO,Tc} - \dot{W}_{h,I}, \quad (5)$$

where  $\Delta H_{ZnO,Tc}$  is the enthalpy of formation of solid ZnO from Zn vapor and  $O_2$  at the temperature at which Zn in the product stream condenses.

The temperature  $T_c$  depends, of course, on the pressure. Also

$$\dot{Q}_{h,II} = -\dot{n}_{ZnO,5} \Delta H_{ZnO,Tc} - \dot{W}_{h,II} \quad (6)$$

and

$$\dot{Q}_{h,III} = -\dot{n}_{ZnO,5} \Delta H_{ZnO,Tm} - \dot{W}_{h,III} \quad (7)$$

### Net Power

The net power, which measures exactly the work equivalent of the Zn and O<sub>2</sub> produced and, to a very close approximation, the net Zn production rate is the difference between the power of the fuel cell and the power required by the electrolysis cell.

### Thermal Efficiency

The thermal efficiency of our process is defined as  $\eta = \dot{W}_{net}/\dot{Q}_h$  and may be compared with the Carnot efficiency to evaluate the importance of the irreversibility associated with the heat exchanger.

### RESULTS

Figures 4-6 are maps which show  $\dot{W}_h$ ,  $\dot{Q}_h$ , and  $\eta$  in  $T_h$ -P coordinates. The ZnO feed rate is 1 mole/sec.

Figure 4 shows lines of constant electric power supply to the electrolysis cell. In Region I, very little electric power is required. Condensed phase ZnO is thermodynamically unstable in this region. We do not now anticipate that Region I will be an acceptable candidate for the process because of the mechanical difficulty of designing and constructing a device for bringing about the electrolysis. However, it is conceivable that, in a suitable solvent, ZnO might be electrolyzed from the liquid phase in this regime, since the activity and Gibbs function of ZnO in solution would be the same as those of the vapor with which it is in equilibrium; the lines of constant electric power requirement would also apply to such a device.

The demand for electric power increases as the temperature goes down or as the pressure goes up in Regions II and III.

Figure 5 shows lines of constant process heat. Inasmuch as the sum of the process heat and the electric power are linked by the requirement that the net energy flow to the device, including that which is transferred at ambient temperature, be equal to the ambient temperature difference between the enthalpy of the products and that of the reactants, lines of constant process heat, except in Region I, approximately parallel lines of constant electric power, but their magnitudes shift in the opposite direction.

Figure 6 shows lines of constant thermal efficiency. In Region I, the thermal efficiency does not depend very strongly on either temperature or pressure. In Regions II and III, the thermal efficiency increases with electrolysis cell temperature, as expected. It is noteworthy, however, that thermal efficiencies in Region III are substantially higher than those in Region II at comparable temperatures and pressures and that, at a given pressure, efficiencies in Region III are substantially higher than those in Region II even though the temperature in Region II is substantially higher than the temperature in Region III. As a matter of fact, even though Region II extends to 2240 K, nowhere in Region II does the thermal efficiency go as high as it is, even at temperatures as low as 1500 K, in Region III. This result, as we have previously noted, follows because the Zn vapor produced in Region II is poorly matched for heat exchange with the reactant feed in the heat exchanger. The suggestion is pertinent that, in a real device for high-temperature electrolysis, the heat exchanger should be used as a source of heat for a heat engine to produce power for the electrolysis cell. In this manner, it is conceivable that such processes might well become all-solar processes.

### CONCLUSIONS

High-temperature electrolysis which uses sunlight as a source of high-temperature process heat is attractive for reducing the amount of electric power and fossil fuel needed for the winning of metals from their ores. The properties of ZnO make it an interesting candidate for use in existing solar furnace facilities to begin the exploration of a new technology, as well as for eventual industrial exploitation.

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# FIGURE CAPTIONS

Fig. 1. Variation, with temperature, of the required ideal total energy ( $\Delta H$ ), electrical energy ( $\Delta G$ ), and process heat for the production of one mole of Zn from ZnO.

Fig. 2. Schematic diagram of an idealized archetypal device for the solar-augmented electrolytic production of Zn and  $O_2$  from ZnO. The circled numbers are stations referred to in the text. The pressure is the same everywhere in the device. Zinc oxide at 298.15 K enters the counter-current heat exchanger at station 5. After having been pre-heated by the descending products in the heat exchanger, it enters the electrolysis cell at station 1. Since the temperature at station 1 must be less than the temperature of the electrolysis cell ( $T_h$ ), process heat is added to it in an amount sufficient to bring its temperature to  $T_h$  in the cell. Electric power is supplied to the cell in an amount sufficient to electrolyze the ZnO to Zn (which emerges from the cell at station 2x) and  $O_2$  (which emerges at station 2y). Process heat, in an amount  $|\Delta H - \Delta G|$ , is added to the cell to keep its temperature constant. The products descend through the heat exchanger, pass through a cooler, if necessary, and are collected. In our analytical study, we have chosen to use as an intellectual construct the indicated ideal fuel cell. It is a device which measures the amount and quality of the Zn and  $O_2$  which have been produced and expresses the result in terms of their work-equivalent. When the work-equivalents of the

products are expressed in this way, the process may be evaluated by comparison with a Carnot engine operating between the same two temperatures, and its thermal efficiency may thus be compared with the thermal efficiency of an ideal device.

Fig. 3. Map in  $T_h$ -P coordinates of operational regions for the solar-augmented electrolysis of ZnO.

Fig. 4. Map on  $T_h$ -P coordinates, which shows lines of constant electric power supply (kW) to the electrolysis cell in the various operating regimes. The ZnO feed rate is 1 mole/sec.

Fig. 5. Map on  $T_h$ -P coordinates, which shows lines of constant process heat (kW) in the various operating regimes. The ZnO feed rate is 1 mole/sec.

Fig. 6. Map on  $T_h$ -P coordinates, which shows lines of constant thermal efficiency in the various operating regimes. The ZnO feed rate is 1 mole/sec.

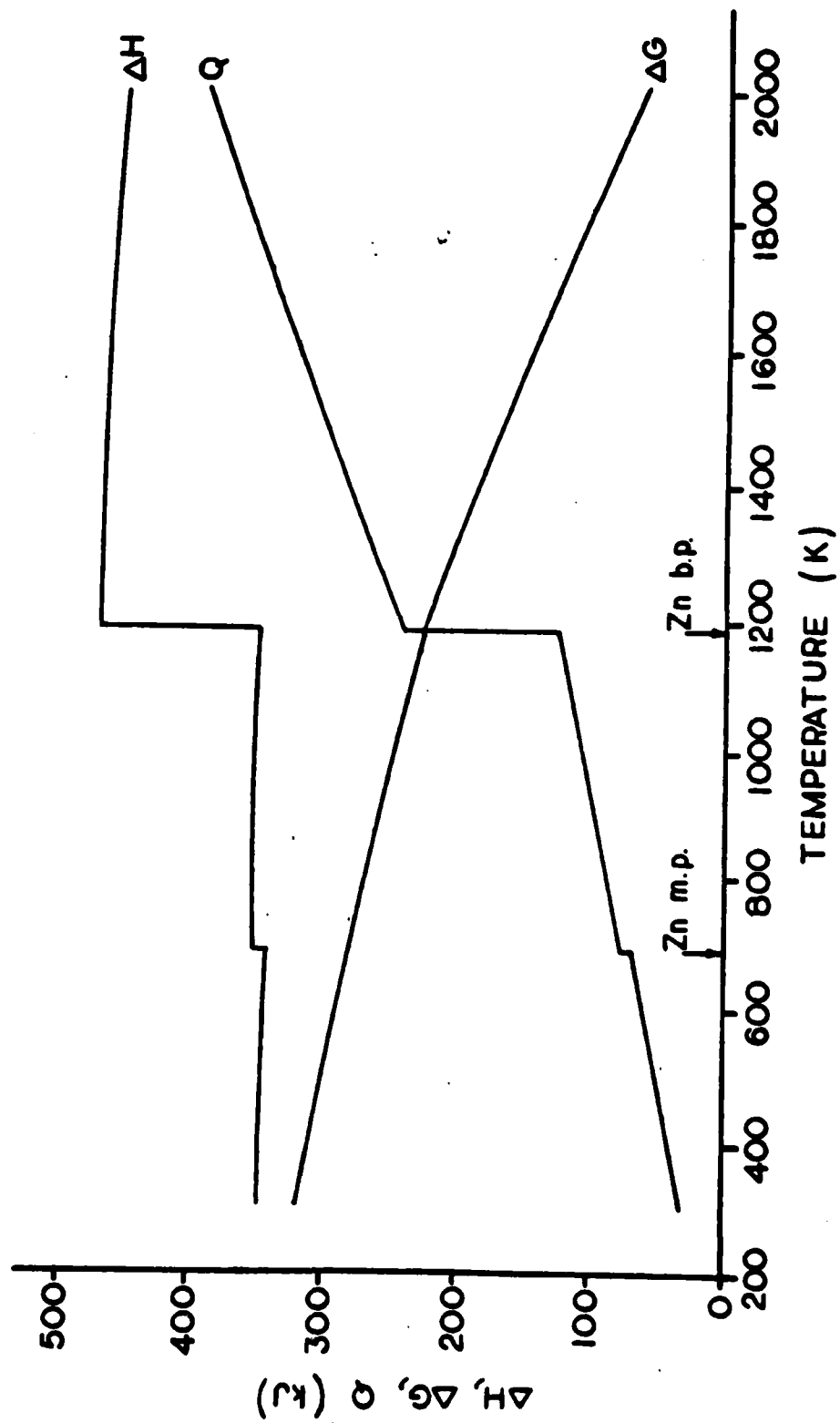


Fig. 1 Fletcher and Noring

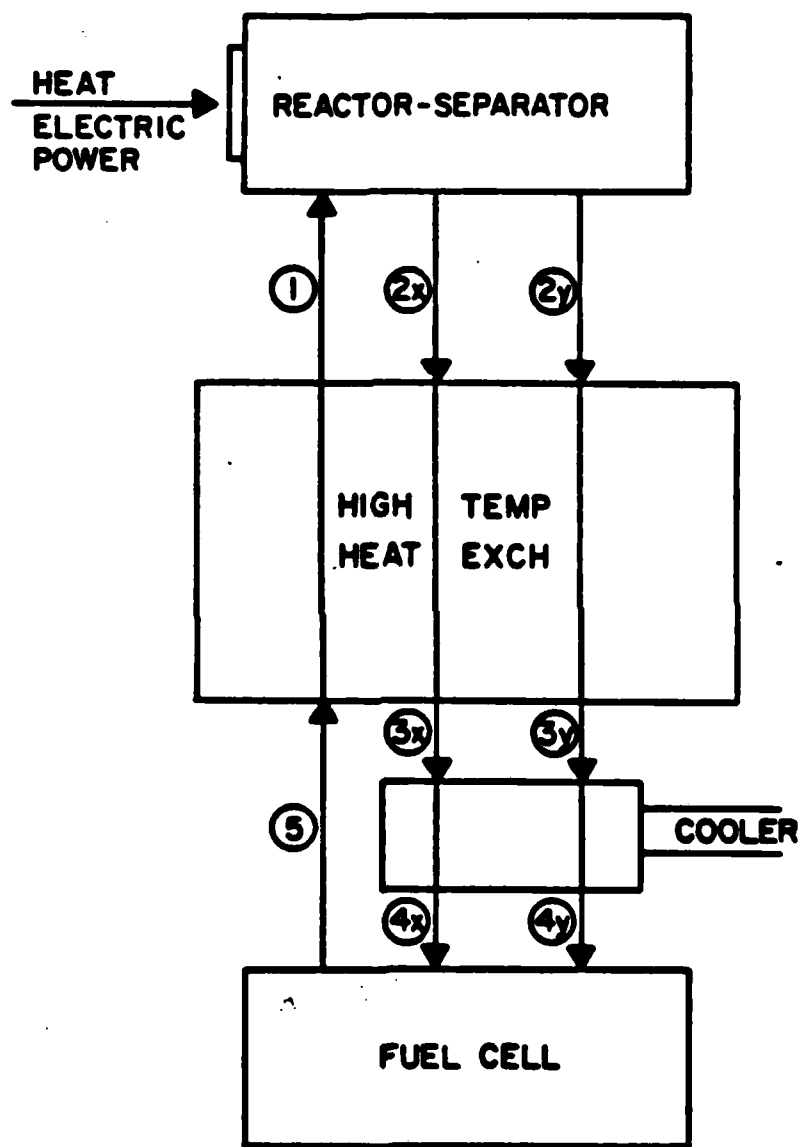


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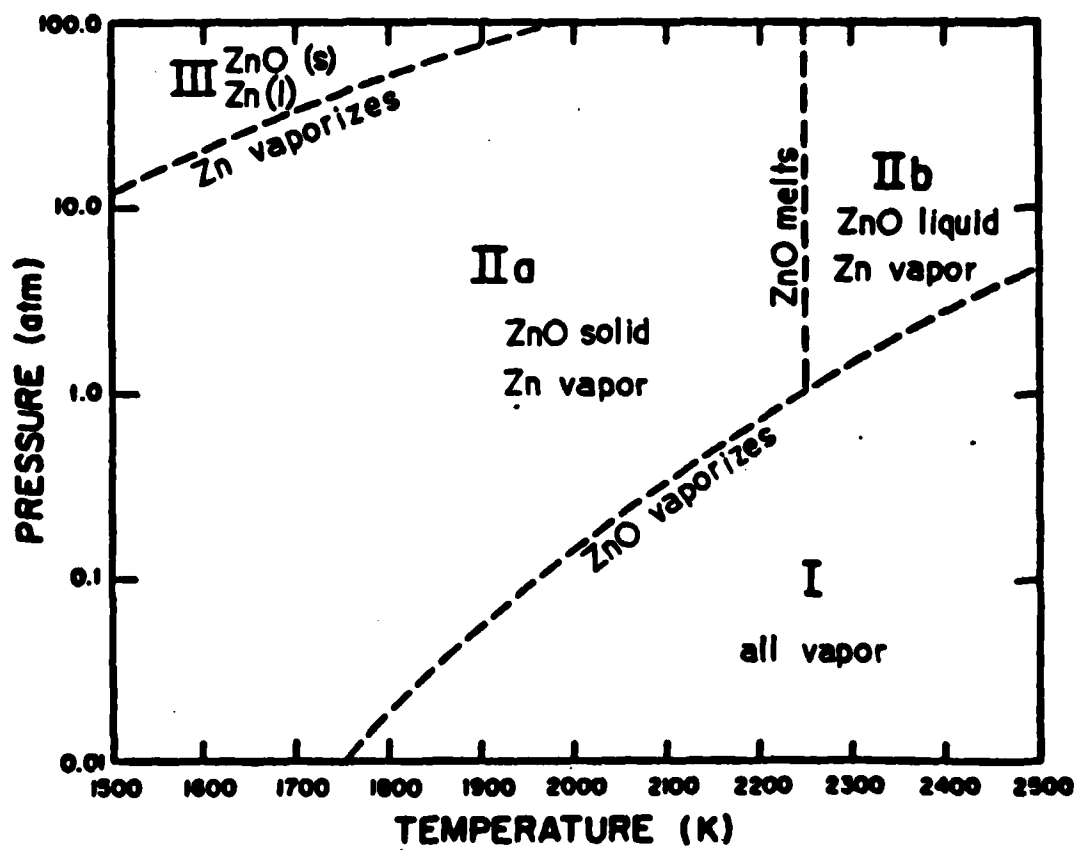


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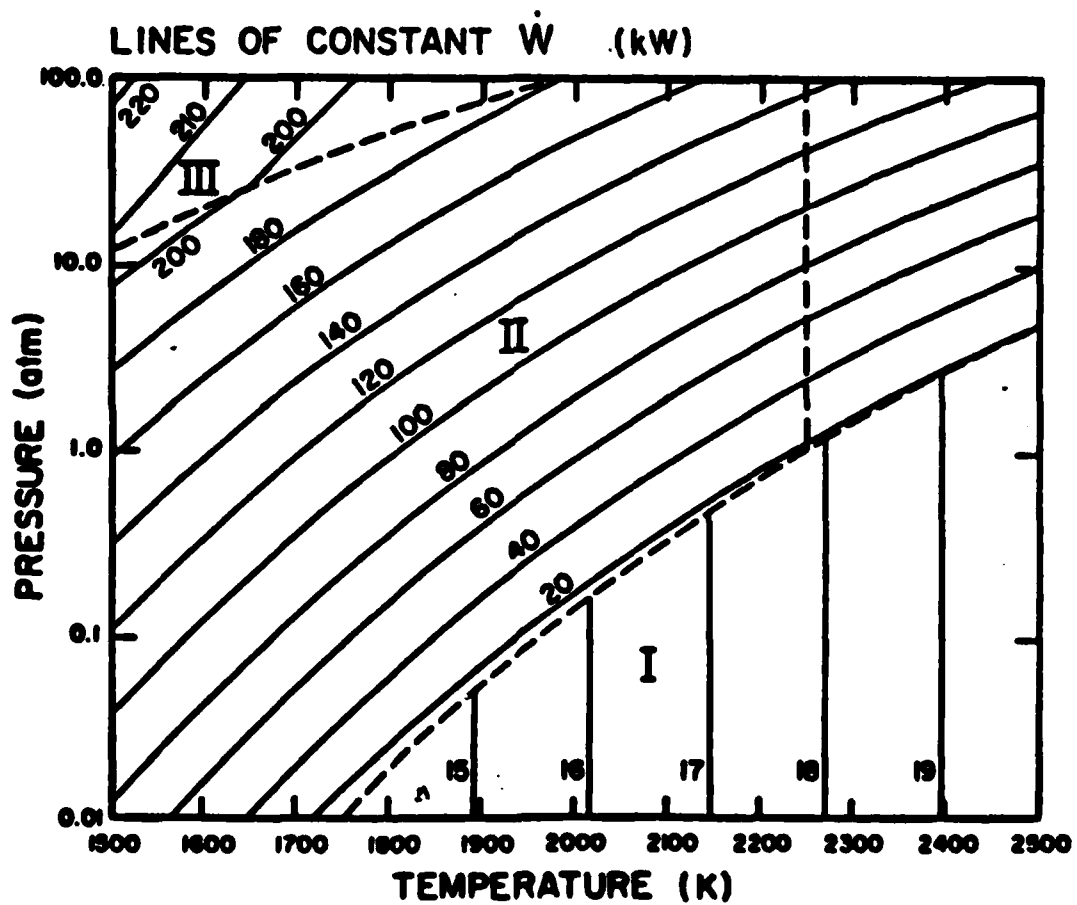


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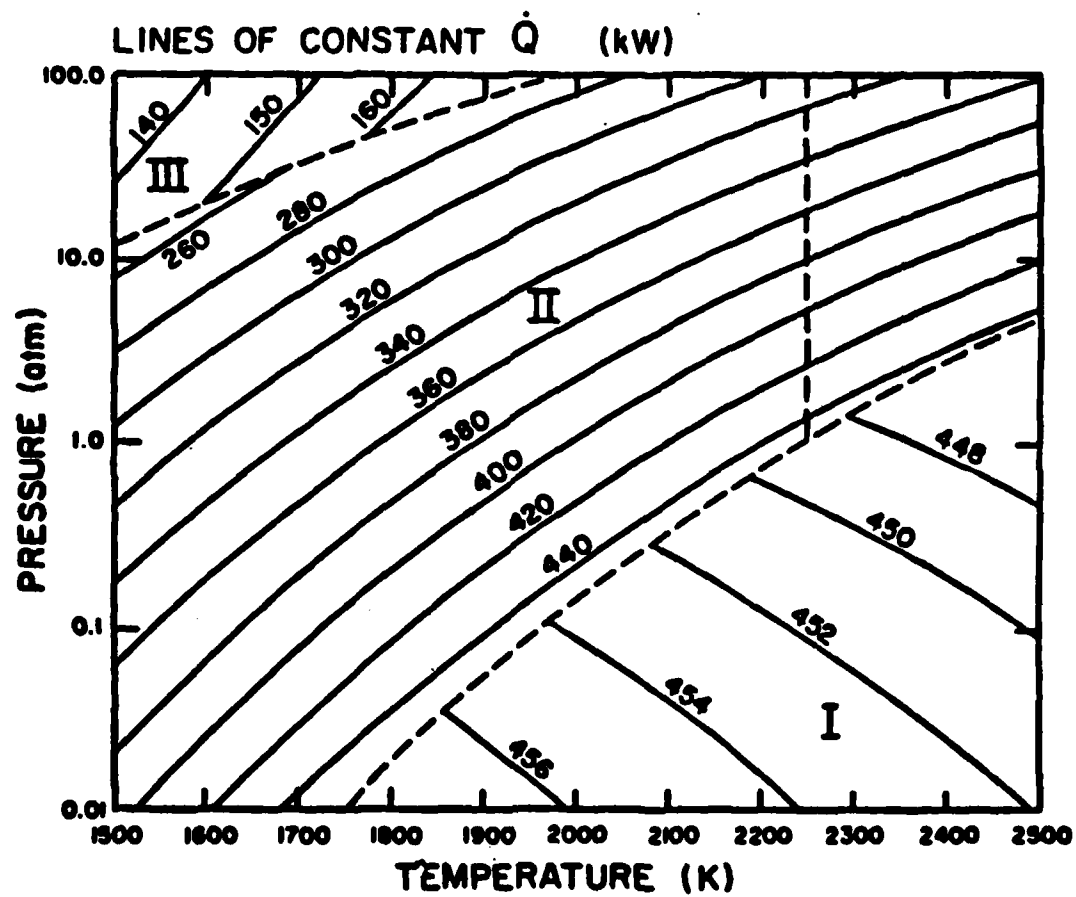


Fig. 5 Fletcher and Noring

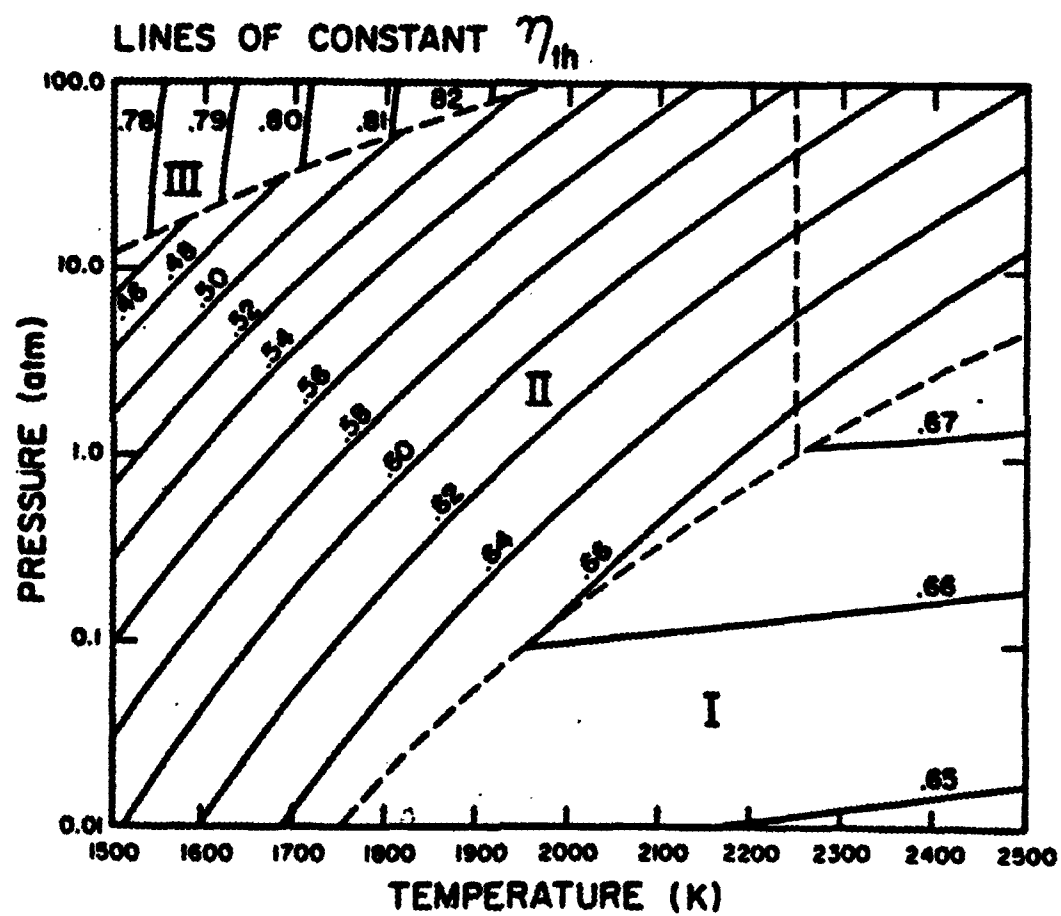


Fig. 6 Fletcher and Noring